

Growth and morphology of organic thin films

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INTRODUCTION

Organic thin films have attracted enormous attention in several respects, one of them being the big advantage of producing cheap and large scale electronic devices. In particular, organic light emitting devices (OLEDs) are already produced and there is an increasing interest in producing organic field effect transistors (OFETs). High charge carrier mobilities are an important prerequisite for ultimate device performance and thus the structural properties of the organic films have to be optimized. So far, we have studied the growth mechanisms of large organic molecules on metal substrates where we could control the growth by the orientation of the substrate as well as by the preparation conditions [1,2]. However, due to the covalent bonding to the metal substrate, the molecules are forced into a coplanar geometry, in most cases, to the substrate surface. Since the transport of electrons or holes is favored along the π -stacking direction, in an OFET device one would prefer perpendicular orientation of the molecules. Furthermore, in order to operate an OFET the gate electrode must be insulated from the electrically active material and therefore, growth on insulators are preferable.

We have investigated thin films of TCNQ and $\text{Cu}(\text{TCNQ})_2$ using the scanning transmission x-ray microscope at BL 5.3.2 (polymer STXM) to monitor the morphology and molecular orientation in ultrathin organic films. TCNQ is one of the molecular components of the first organic superconductor TTF-TCNQ and is known to form radical anion charge transfer complexes with a number of different metals.

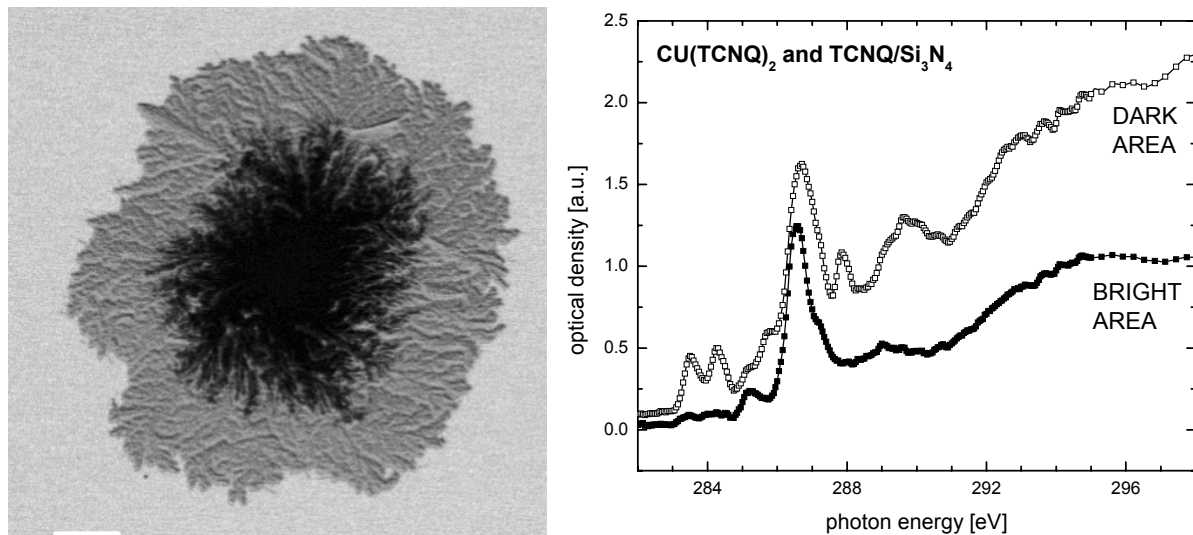


Fig. 1 shows a typical image of vacuum sublimated films prepared by co-evaporation of TCNQ and Cu on Si₃N₄ membranes (membrane thickness: 100 nm, nominal film thickness: 80 nm). We observe structures with a diameter of up to 40 nm and mainly two different grey shades, which are attributed to two distinct film thicknesses. The internal structure is due to the dendritic growth. Microspectroscopic analysis of the different areas reveals, that the stoichiometric properties are obviously not identical (see Fig. 1 right). Closer inspection of the spectra reveals, that the brighter areas consist of Cu(TCNQ)₂, whereas the darker areas consist of unreacted TCNQ [3]. The only plausible explanation is, that unreacted TCNQ segregates to the surface leaving the charge transfer salt underneath. A comparison of the absorption spectra with those recorded from TCNQ and TCNQ-based charge-transfer complexes epitaxially grown on metal substrates [3], indicates that in the brighter areas (corresponding to the charge-transfer complex), the molecular plane is coplanar with the substrate. In the darker areas (unreacted TCNQ), the molecules are likely to be oriented upright, i.e. in the favorable configuration of an OFET.

Of course, one major problem still remains to optimize the film growth for potential device application: how can one control the homogeneity of the films? One possibility is the use of well defined nucleation centers, e.g. patterning of the substrate with metallic nanowires (which also could be utilized as contacts for charge carrier injection). This has been tested for in-situ growth of NTCDA on SiO₂ at PEEM-2. However, preparation at room temperature results in a very high molecular mobility (note that the structures in Fig 1. are more then 100 µm apart !) and therefore, step edges do not act as a uniform nucleation centers but they are arbitrarily overgrown by organic microcrystals. We rather favor lower substrate temperatures and significantly reduced sublimation rates for uniform film growth – in optimum cases perfect layer-by-layer growth as demonstrated on Ag single crystals [4].

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